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Analytical Investigation of Fuel Cells by Using In-situ and Ex-situ Diagnostic Methods

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Abstract. The study of the behaviour of fuel cells by using various in-situ and ex-situ diagnostic methods is a main topic at the German Aerospace Center (DLR). The degradation of cell components of polymer electrolyte fuel cells (PEFC, DMFC) and of solid oxide fuel cells (SOFC) are of special interest. For this purpose physical and electrochemical methods are used individually as well as in combination. In addition to routinely applied electrochemical methods different methods for locally resolved current density measurements by means of segmented cell technology and integrated temperature sensors have been developed. The latest development with segmented bipolar plates based on printed circuit boards (PCB) is used both in single PEFC cells and stacks. Furthermore, a measuring system for segmented SOFC cells has been developed allowing for the spatially resolved characterisation of cells in terms of current density/voltage characteristics, impedance spectroscopy data, operating temperature and gas composition. The paper summarises the capabilities at DLR with respect to the analysis of fuel cells' behaviour and gives examples of analytical studies to discuss the potentials and limitations of the diagnostic methodology that is applied.

Introduction

In order to optimise the operational behaviour, lifetime and costs of fuel cells and minimise cell degradation it is very useful to apply in-situ and ex-situ analytical methods. The application of advanced diagnostic methods by monitoring cell characteristics under real operating conditions can provide valuable information to be used for the development of degradation mitigation strategies. DLR Stuttgart is working for many years on alkaline fuel cells (AFC), polymer electrolyte membrane fuel cells (PEMFC), direct methanol fuel cells (DMFC) and solid oxide fuel cells (SOFC). Special emphasis in the development of the different fuel cell types is laid on the understanding of the fuel cell processes and the degradation phenomena occurring under specific local operating conditions. For this purpose, different in-situ diagnostic methods with spatial resolution by means of segmented cells have been developed [1, 2] and applied in combination with ex-situ methods such as SEM/EDX, XPS, XRD, TPDRO, porosimetry etc. [3,4]. These investigations aim at the determination of local effects and the identification of critical operating conditions during technically relevant operation. The paper summarises the capabilities at DLR for the analysis of fuel cells and shows exemplary results of analytical studies performed in recent years.

Spatially resolved measuring technique for PEFC/DMFC

In order to better understand the reactions and mechanisms inside a fuel cell as well as the local operating conditions in-situ measuring techniques to determine the current density distribution in PEFC and DMFC were developed at DLR Stuttgart [1]. These techniques are used successfully to advance and to support the development of fuel cell stacks. Furthermore, the current density distribution measurements can also be used as a feedback control system to optimise the operation conditions, to avoid unfavourable conditions and to detect problems and defects at an early state. Various techniques for the measurement of current density distributions were developed. In all techniques at least one of the flow fields is segmented.

In a first design the individual segments were connected together with external resistances which are used for the measurement of the current density. This design is only suitable for the current density measurements in end plates of stacks or in single cells. In a following approach hall sensors were used to determine the current inside the segments. The actual development uses a design in which the segments as well as the resistances are realised in a printed circuit board (PCB) which can be used as a bipolar plate in stacks as well as in single cells. Results can be used to validate models and to optimise components of a stack, e.g. flow field and manifold design, as well as the operating conditions of fuel cells. The following figure shows the principle of the measuring technique using printed circuit board technology.

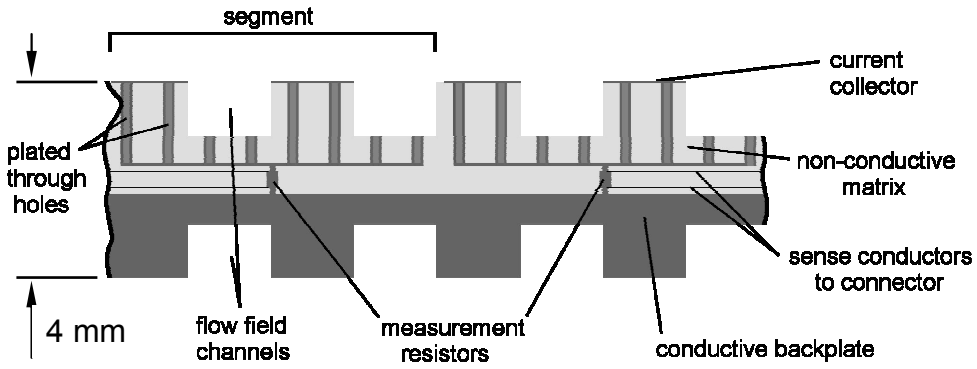

Fig 1: Principle of PCB segmented cell technique

The major challenge of the technique in the development of control strategies based on current density measurements is its interpretation. In combination with the electrochemical impedance spectroscopy (EIS) it is possible to determine mechanisms and to speed up the optimisation of durability and lifetime. The board which is used as a real bipolar plate inside a fuel cell or fuel cell stack is shown in Fig. 2.

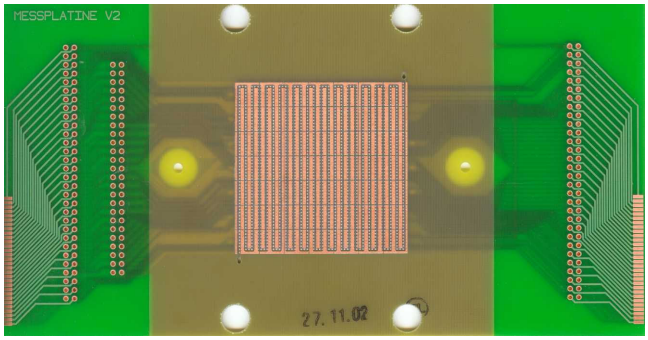

Fig. 2: Printed circuit board (PCB) as segmented bipolar plate with 49 segments with an integrated flow field for use in single cells and stacks (25 cm^2 active area)

Investigations of fuel cells with ex-situ methods

The electrochemical performance and the fuel cell behaviour which is determined by the in-situ methods are the critical properties for the users of fuel cells, but not necessarily sufficient for the development of fuel cells and fuel cell components. For the development of fuel cells the physical properties, mainly structure and composition, as well as the dependence of the physical properties from the manufacturing parameters are of equal importance. The investigation of the physical properties is not only interesting for the fuel cell development, but also for the understanding of degradation processes. It is essentially necessary to obtain information about alterations of the fuel cell components. In-situ methods allow for studying alterations in the performance as well as in the fuel cell behaviour, but they do not give information about the reasons for these alterations. In contrast, by using ex-situ methods the alterations of fuel cell components can be identified on different levels depending on the used methods, e.g. alterations in the structure can be integrally determined by porosimetry and visualised by scanning electron microscopy (SEM). The alterations in the composition of fuel cell components can be analysed by various methods: surface analytical methods, like X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, ion scattering spectroscopy or secondary ion mass spectrometry, yield information about the chemical composition of the surface (few nm); with energy dispersive or wavelength dispersive X-ray spectroscopy the chemical composition of the samples can be investigated in a region near the surface (approx. 1 µm). In addition, many other methods can be used for the analysis of the chemical composition or of other physical properties.

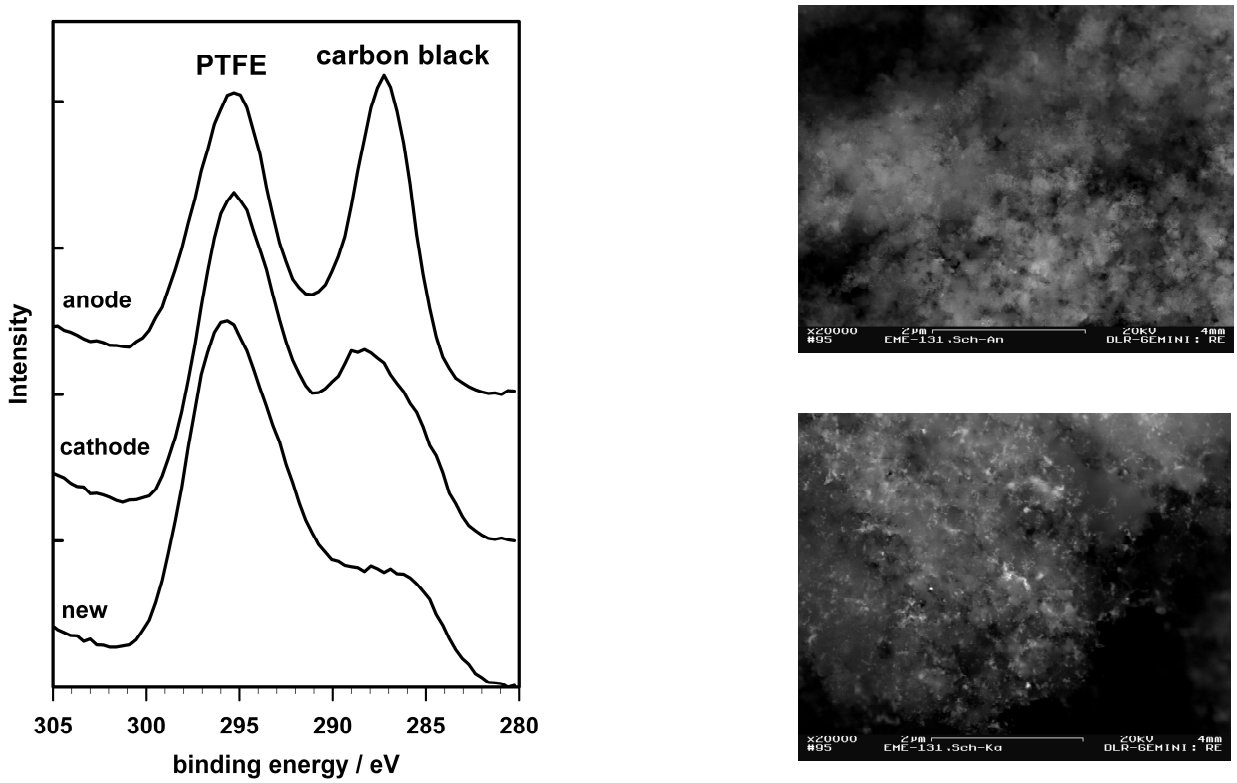

Fig. 3: Left side: XPS investigation of the decomposition of the PTFE due to fuel cell operation [5]; right side: SEM investigation of the platinum agglomeration during the fuel cell operation (on top: used anode, bottom: used cathode).

Fig. 3 shows the results of the ex-situ characterisation performed in a degradation study of PEFC. The XP spectra on the left side in the figure clearly indicate that the poly-tetra-fluor-ethylene (PTFE), which is used to give the electrodes hydrophobic properties, is partially decomposed. The

PTFE decomposition is more pronounced in the anode than in the cathode. Consequently, related to the PTFE decomposition, the hydrophobicity in the anode is significantly reduced, whereas the hydrophobicity of the cathode is only slightly affected. The SEM images depicted on the right side in Fig. 3 show an agglomeration of the platinum catalyst in the cathode, whereas the distribution of the platinum in the anode is not significantly changed in comparison with a new electrode. The catalyst surface area, which is active for the fuel cell reaction, decreases caused by this catalyst agglomeration

Both alterations in the electrodes, PTFE decomposition and catalyst agglomeration, influence the fuel cell performance and fuel cell behaviour. As a consequence of catalyst agglomeration the performance decreases and as a consequence of the PFTE decomposition the fuel cell behaviour related to the water management is changed. Both phenomena were observed in the in-situ measurement and could be quantified by electrochemical impedance spectroscopy measurement; but the reasons for this behaviour could only be identified by means of the ex-situ investigation methods.

Spatially Resolved Measuring Technique for SOFC

Experimental Details. The set-up of the measuring system with segmented cells is schematically shown in Fig. 4. Square-shaped cells with an area of 100 cm² which are divided into 16 segments with an active area of 4.84 cm² each, are integrated in a metallic cell housing and sealed with glass seal. The metallic housing is also subdivided into 16 galvanically isolated segments with an active area of 73.96 cm². In order to determine the temperature at each segment allowing for correlating experimental data such as voltage, current density and impedance data with the local temperatures, thermocouples are introduced in the metallic segments. Additionally, 16 capillaries are integrated to collect samples of the anode gas to be analysed by gas chromatography. The method is quite flexible with regard to the integration of different cell designs: metal-supported cells (MSC) as they are developed and fabricated at DLR according to its spray concept [6] as well as electrolyte- (ESC) and anode-supported cells (ASC) can be characterised. With MSC and ASC cells only the cathode is segmented, whereas ESC cells are segmented on both the anode and the cathode side. More details on the measuring system are given in [2].

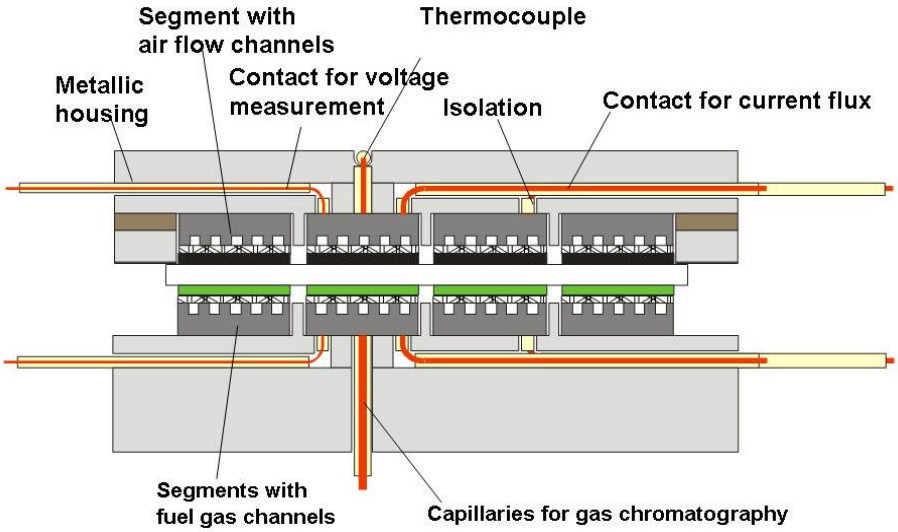

Fig. 4: Set-up of measuring system for the characterisation of segmented cells with both cathode and anode segmentation

Results and Discussion. The measuring system described has been applied to locally characterise SOFCs with the segmented cell arrangement. Two examples are given to demonstrate the potential of this spatially-resolved measuring technique. As a first example the power density distribution over the 16 segments, each 4.6 cm^2 wide, of a plasma-sprayed metal supported cell (100x100 mm^2) is shown in Fig. 5 for an operating temperature of 800 °C [7]. The gas flow rates are 12.5 sccm/cm^2 H_2, 12.5 sccm/cm^2 N_2 as fuel and 80 sccm/cm^2 air as oxidant. The current density distribution varies tremendously over the cell. Maximum differences of 116.6 mW/cm^2 could be identified in Fig. 5. The worst segment reaches only 23.6 % of the power density of the best segment. The average power density of the cell was 125.6 mW/cm^2 at 0.7 V. In some segments (e.g. segment 4 and 16) a significant lower power density is observed probably due to a glass sealing failure. There is a slight increase of the power density of about 15.1 % in average over all segments from air inlet to air outlet. The main effect could be attributed to the inhomogeneous gas distribution at the inlet and to the sealing. The differences in the electrochemical behaviour are also caused by local water production as a result of the slightly permeable electrolyte. It could be seen by local impedance spectroscopy that the current distribution is in good accordance with the local resistances. The local temperatures directly affect the ohmic resistances and should therefore be taken into account.

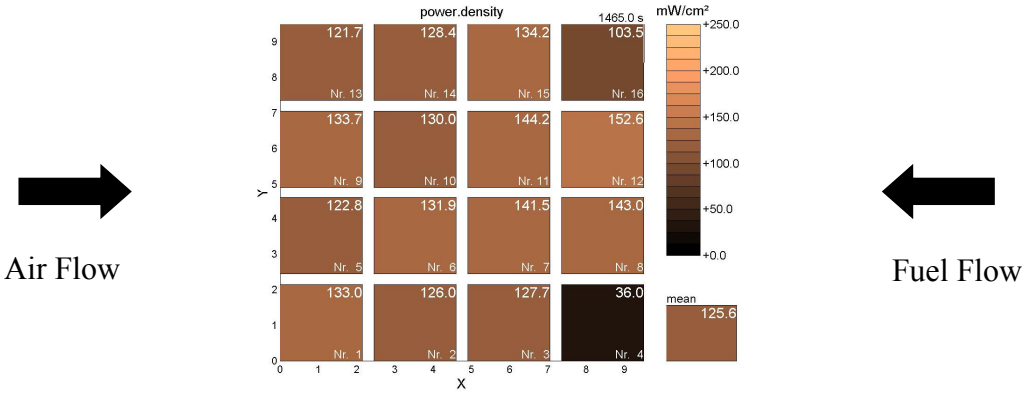

Fig. 5: Power density distribution of a plasma sprayed cell with 0.7 V cell voltage in average

The experiments revealed that the anode overpotential at an overall cell voltage of 0.7 V with the selected gas supply is very small and can be neglected without major error. As a consequence, the overpotential is mainly related to the cathode and further cell improvement should concentrate on improving performance of the oxygen reduction reaction. The results obtained by these measurements show a variation of the behaviour of the cell along the flow path. Current density, impedance and temperature can be associated with the observed effects. The obtained data can be used to avoid critical temperature gradients during operation and also to optimise functional layers to homogenise current density and heat production especially in a fuel cell stack.

The second example which is presented covers the operation of an anode-supported cell (ASC2 from InDEC, Netherlands) with a reformate composition as the fuel gas and the electrochemical reaction of the fuel gas components along the flow path [8]. The ASC cell contains a 540 µm thick NiO/YSZ anode with a thin anode functional layer, a 7 µm thick 8YSZ electrolyte, a 7 µm thick YDC interlayer and a 30 µm thick LSCF cathode. A spatially resolved measurement along the flow path of the fuel with a realistic reformate composition (54.9 % N_2, 16.7 H_2, 16.5 % CO, 6.6 % CH_4, 2.2 % CO_2, and 3.2 % H_2O) was performed to investigate the processes taking place in more detail. The influence of the area-specific load on the power density and the fuel utilization at operation of a segmented ASC2 cell (counter flow) along a row of segments (segment 9-12) with fuel inlet at segment 9 is shown in Fig. 6. The results in Fig. 6 reveal an excellent conversion of CO- and CH_4-containing fuel gas with 78.1 % at 400 mA/cm^2 and with 83.9 % at 435 mA/cm^2 at the fuel exit. At a current density between 0 and 200 mA/cm^2 the power density decreases only slightly along the flow path, but at a load of 400 mA/cm^2 a quite significant and strong reduction of power density at

the fuel exit (segment 12) was observed. This behaviour is even more pronounced at a further increased current density of 435 mA/cm² of the total cell, segment 12 now shows a very low power density. It seems that the increasing conversion rate at the segments 9–11 causes performance reduction at segment 12 that could result in critical conditions and hence enhanced corrosion at the fuel exit.

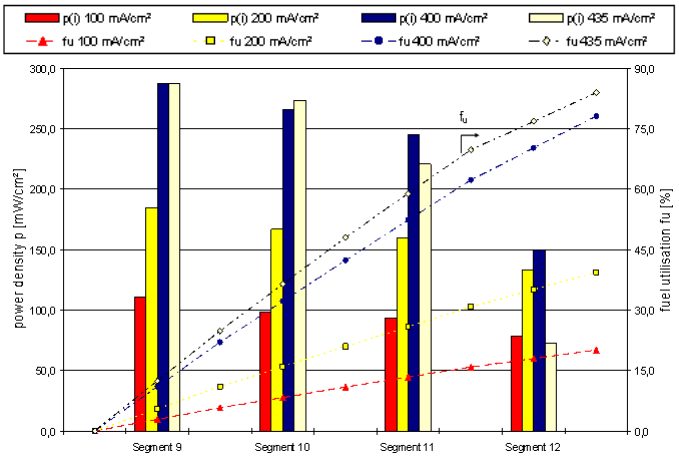

Fig. 6: Comparison of power density and fuel utilisation along the flow path during variation of the area-specific load of a ASC2 cell (active area: 73.96 cm²) during operation with reformate gas; counter flow mode, fuel gas inlet at segment 9, fuel gas outlet at segment 12; current density equivalent: 0.552 A/cm^2, air flow rate: 0.02 slpm/cm^2.

Summary

The measuring techniques and exemplary results that are presented prove that it is possible to identify different degradation mechanisms and to optimise operating conditions in fuel cells. In order to overcome the remaining challenges in fuel cell development (performance, durability, reliability and costs) it is of paramount importance to apply sophisticated analytical methodology for improving the understanding of fuel cell systems.

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